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Abstract

We report the electrochemical potentials at which localized pitting and repassivation occur on icosahedral Al-Cu-Fe, and on a series of related alloys and elemental metals. The electrochemistry occurs in a buffered NaCI solution, pH 8.4. Under these conditions, pitting and repassivation appear to be controlled mainly by the chemical composition of the alloy, although the quasicrystalline phase displays an anomalous resistance to repassivation. Corrosion of this phase proceeds by dissolution of Al and Fe, leaving behind pits which are Cu-enriched.

ELECTROCHEMICAL PITTING AND REPASSIVATION ON ICOSAHEDRAL AL-CU-FE, AND A COMPARISON WITH CRYSTALLINE PHASES

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Abstract

We report the electrochemical potentials at which localized pitting and repassivation occur on icosahedral Al-Cu-Fe, and on a series of related alloys and elemental metals. The electrochemistry occurs in a buffered NaCl solution, pH 8.4. Under these conditions, pitting and repassivation appear to be controlled mainly by the chemical composition of the alloy, although the quasicrystalline phase displays an anomalous resistance to repassivation. Corrosion of this phase proceeds by dissolution of Al and Fe, leaving behind pits which are Cu-enriched.

Introduction

The process of localized corrosion is important to the failure of materials, particularly in liquid environments.

Pitting corrosion typically begins at defects on the surface of a material.[1] The oxide layer is removed by increasing the electrochemical potential at the metal (during voltammetry). This causes the metal to be exposed, and the metal dissolves away, creating a pit which emanates radially from the defect. The potential where pitting begins corresponds to a sudden increase in electrochemical current. A more positive pitting potential indicates higher resistance to this localized corrosion. Similarly, as potential decreases during voltammetry, an oxide re-forms on the surface and re-passivates. This is signalled by an abrupt decline in electrochemical current. The value of the repassivation potential is related to the ability of the exposed metal to reform the passive oxide layer, which is also important to corrosion resistance.[1] A more positive repassivation potential indicates easier formation of the passivating layer.

Hence, the pitting and repassivation potentials during cyclic voltammetry serve as indications of the conditions under which these localized corrosion events can occur. Previously, electrochemical corrosion of quasicrystals has been investigated,[2-4] but pitting and repassivation potentials have not been examined.

Experimental Description

Sample preparation. The alloys β, λ, ψ, ω were prepared by hot-isostatically-pressing a gas atomized powder (10-25 μm). The resultant monoliths were cut and polished down to 1 μm diamond paste. They were examined using scanning electron microscopy (SEM) and scanning Auger microscopy (SAM) for secondary phases; none could be detected. (The detection limit is about 0.1% in surface area.) Table 1 shows the bulk composition of each of the alloys; these are determined by inductively-coupled plasma atomic-emission spectroscopy (ICP-AES). The ψ-phase is the quasicrystalline phase. The β, λ, and ω alloys border on the ψ-phase in the phase

diagram, and hence are close chemical analogs (crystalline). Aluminum, copper and iron were polycrystalline samples that were cut and polished similarly.

Electrochemical Parameters. The potentiostat was an EG&G Princeton Applied Research #273 potentiostat, used with a Keithley #194A voltammeter. The three-electrode system consisted of a SCE reference electrode, a platinum counter electrode, and the sample as working electrode. The scan rate was 5 mV/s from -1.2 volts to 0.2 V. In the case of Cu, the upper limit for the potential was extended to 0.3 V. The solution was aqueous 0.1 M NaCl, buffered with boric acid/borate to pH 8.4. Nitrogen was bubbled through the solution before and during electrochemistry.

Metal	V_{pit}	N_{pit}	V_{rp}	N $_{rp}$	ΔV_{av}	% Al	% Cu	% Fe
Cu	+0.22	1	+0.21	1	0.01		100	
Al	-0.486 ± 0.018	5	-0.733 ± 0.056	4	0.25	100		
Fe	-0.184 ± 0.043	5	-0.672 ± 0.059	5	0.49			100
β-Al-Cu-Fe	-0.137 ± 0.043	6	-0.270 ± 0.029	3	0.13	51.1 ±0.3	34.6 ±1.2	14.3 ±0.3
λ–Al-Cu-Fe	-0.153 ± 0.038	3	-0.457 ± 0.110	3	0.30	74.5 ±0.3	3.0 ±1.2	22.5 ±0.3
ψ-Al-Cu-Fe	-0.194 ± 0.033	8	-0.667 ± 0.014	3	0.47	65.7 ±0.3	22.2 ±1.2	12.1 ±0.3
ω-Al-Cu-Fe	-0.276 ± 0.055	3	-0.470 ± 0.025	3	0.19	69.58 ±0.17	20.27 ±0.2	10.14 ±0.19

Table 1: Measured pitting and repassivation potentials, and chemical compositions, of the metals. The pitting potentials, V, are measured vs. a saturated calomel electrode (SCE). The uncertainties are 95% confidence intervals. The number of measurements is N. The difference between the average values of V_{pit} and V_{rp}, ΔV_{av}, indicates the width of the hysteresis illustrated in Fig. 1. Compositions are given in atomic per cent.

Experimental Results

Typical Voltammogram. Figure 1 shows a typical cyclic voltammogram. During the positive-going sweep, the curve shows a low and constant value between the initial potential of -1.2 V and -0.25 V. At -0.25 V the current density starts to increase quickly to a final value of +16.5 mA/cm² at 0.2 V. The potential corresponding to the change in the slope is the pitting potential, V_{pit}. The pitting potential can be determined more exactly by approximating the baseline (at V<-0.25V) and the increasing current density (V>-0.21V) as straight lines, and extrapolating them to their intersection. In Fig. 1, V_{pit} equals -0.25 V .

After reversing the potential ramp, the curve decreases rapidly between 0.2 V and –0.66 V, then flattens out at –0.66 V. The repassivation potential, V_{rp} is also determined by extrapolation of the two sections of the curve. In this example, V_{rp} equals –0.66 V. The cyclic voltammograms for the other phases show similar behavior; the difference is that the pitting and repassivation potentials are shifted toward positive or negative values.

Pitting potentials. The pitting potentials for the different metals are given in Table 1. These values are negative for all the compounds, except for Cu which shows a positive value,

+0.22 V. (The apparent pitting potential for Cu may actually indicate oxidation [5] or some electrochemical process other than pitting.) The trend in pitting potentials implies that the most corrosion-resistant system is pure Cu and the least resistant is pure Al. The quasicrystalline phase shows an intermediate behavior with a pitting potential of -0.194 V.
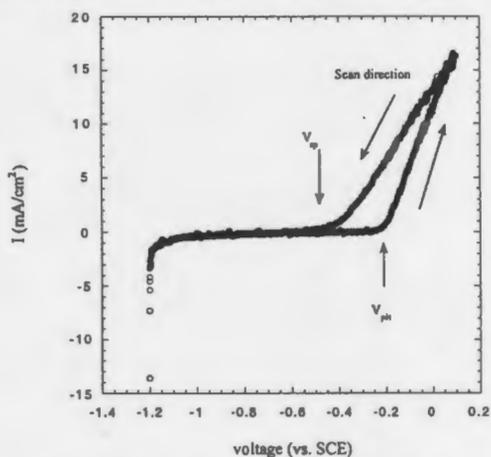

Figure 1. Cyclic voltammogram for ψ-$Al_{65}Cu_{23}Fe_{12}$, showing both a positive- and negative-going sweep.

The pitting potential as a function of atomic concentration of Al and Cu is represented in Figures 2a and 2b, respectively. Figure 2a shows that the pitting potential decreases smoothly with aluminum concentration, and increases smoothly with Cu concentration. The λ-phase, which is poorest in Cu and richest in Fe, falls somewhat outside the trends established by the other metals. We speculate that the reactivity of the λ-phase may be controlled by Fe, rather than by Al or Cu. There is no obvious correlation between V_{pit} and Fe concentration (not shown as a Figure), at least over the range of compositions spanned by these alloys.

Repassivation Potentials. The repassivation potentials were determined for the various alloys. The results are included in Table 1. The repassivation potentials range from +0.21 V for copper to -0.733 V for pure aluminum. The ψ-phase shows an intermediate value, -0.667 V.

Repassivation potentials are shown as a function of atomic composition in Figures 3a and 3b. The same trends are followed as for the pitting potential: the repassivation potential decreases with Al content (Fig. 3a), and increases with Cu content (Fig. 3b). There is little or no correlation with Fe content (not shown). The λ--phase tends to deviate toward more positive values of V_{rp}, as it did also for the pitting potential. Again, this may be related to the low Cu and high Fe content of this phase. An even stronger deviation is shown by the ψ-phase, toward *negative* values of V_{rp}. Note that the ψ-phase did not show such a deviation in the values of V_{pit} (Fig. 2). This is also reflected in the fact that the voltage hysteresis, i.e. the difference between pitting and repassivation potentials, is unusually large in the ψ-phase, relative to the other Al-rich alloys (see Table 1). The more negative potential exhibited by the ψ-phase is an undesirable property, as it signals an unusual resistance to repassivation.
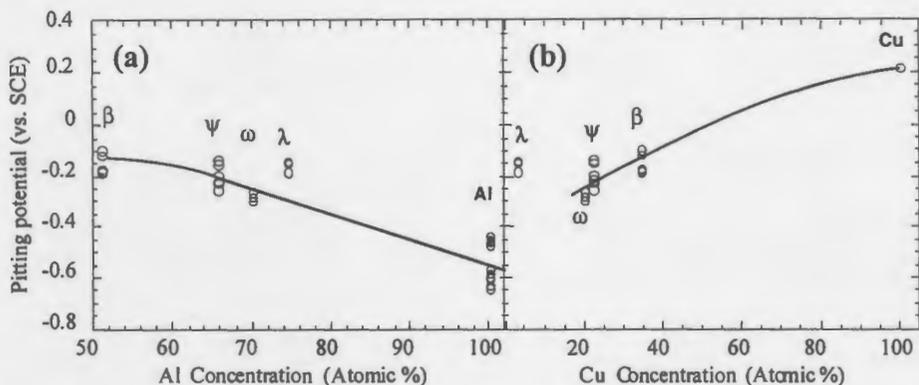
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Figure 2. Variation of pitting potential as a function of bulk atomic concentrations of (a) Al, and (b) Cu. Lines are drawn simply to guide the eye. All experimental values of V_{pit} are shown, corresponding to the averages given in Table 1.
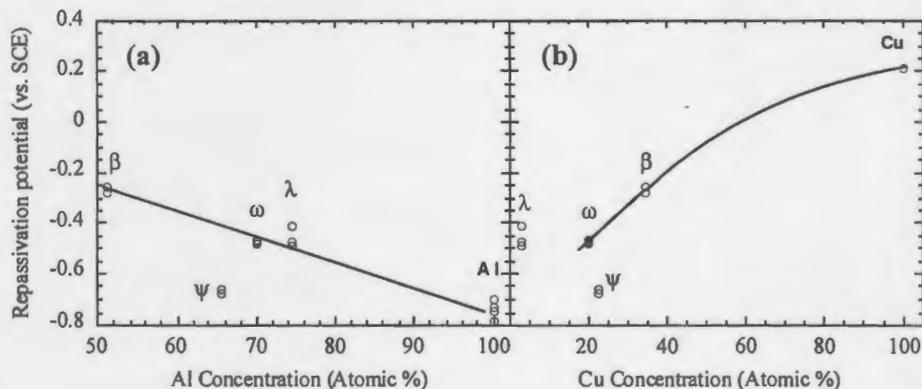

Figure 3. Variation of repassivation potential as a function of bulk atomic concentrations of (a) Al, and (b) Cu. Lines are drawn simply to guide the eye. All experimental values of V_{rp} are shown, corresponding to the averages given in Table 1.

Microscopic and Chemical Analysis of ψ-Phase Pits. A scanning electron micrograph of the pits formed on the ψ–phase is shown in Figure 4. The pits exhibit high contrast relative to the background material, i.e. they are either white or black, and they are about 1 μm in diameter. The boundaries between the powder particles which comprised the sample originally (before hot isostatic pressing) are evident as strings of smaller black dots, which mark the original oxide coating. The pits do not form preferentially at the prior particle boundaries.

Both SAM, and energy-dispersive spectroscopy (EDS) of x-rays generated in SEM, show Cu-enrichment in the pits. SAM, for instance, indicated that the pits contain 35-37% Al, 7% Fe, and 55-58% Cu, whereas the matrix surrounding the pits contains 62% Al, 20% Fe, and

18% Cu. Within the probable limits of accuracy of the SAM measurement (3-4 atomic %), the values for the matrix agree with the values expected for the bulk sample (Table 1). The values for both the matrix and the pits were measured only on a single sample (which underwent one cycle of voltammetry), and for only a few pits. Hence, their precision is uncertain. Nonetheless, they provide a qualitative example of the degree of Cu-enrichment.

This analysis of the pits is consistent with the chemical composition of the solution measured with ICP-AES. The solution after corrosion showed a concentration of 0.24 ppm Al, 0.07 ppm Fe, and no Cu. (The detection limit was 0.05 ppm for all three elements.). Hence, all three analyses (SAM and EDS of the pits, and ICP-AES of the solution) lead to the conclusion that Al and Fe dissolve during cyclic voltammetry, leaving pits which are enriched in the noblest metal, Cu.

These chemical analyses provoke conclusions analogous to those of Asami, et al.,[3] who found that electrochemical corrosion of icosahedral Al-Pd-Mn in media similar to ours left a surface enriched in the noble metal, Pd. Also, Dubois et al. [2] analyzed the solution left after electrochemical corrosion of an Al-Cu-Fe-Cr coating in acidic media. They found very little Cu in solution, implying that the remaining solid surface would be Cu-rich. Hence, the general trend seems to be that the noblest metal remains at the surface during corrosion, while the other components dissolve.
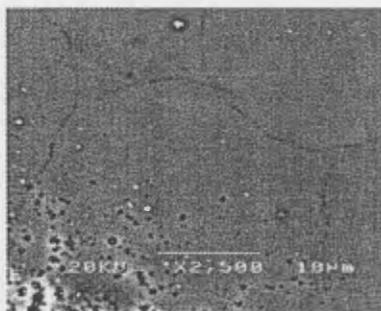

Figure 4: Scanning electron micrograph (2500x) of the ψ-phase after cyclic voltammetry. The pit concentration increases toward the lower left corner. Particle boundaries are evident as strings of small dark dots. The horizontal white line at the bottom of the figure corresponds to a length of 10 μm.

Conclusions

Among the alloys examined here, the propensity for electrochemical pitting appears to be controlled mainly by chemical composition. Resistance to corrosion is enhanced with decreasing Al content, and with increasing Cu content. There is no apparent correlation with Fe content, over the range of metals examined here. Repassivation potentials follow a similar trend, although the icosahedral phase shows an anomalous resistance to repassivation. The pits on the icosahedral phase are Cu-rich, apparently forming by dissolution of Al and Fe.

Our conclusion that corrosion is controlled mainly by chemical composition, is quite similar to that of Massiani, et al.[4] They found that the resistance to electrochemical corrosion as a function of pH, in a series of Al-Cu-Fe alloys, was a function of their composition rather than their specific atomic structure.

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